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► To cite this version:

A. Zahn, P. Franz, C. Bechtel, J.-U. Grooss, T. Röckmann. Modelling the budget of middle atmospheric water vapour isotopes. *Atmospheric Chemistry and Physics*, 2006, 6 (8), pp.2073-2090. hal-00295940

HAL Id: hal-00295940

<https://hal.science/hal-00295940>

Submitted on 20 Jun 2006

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Modelling the budget of middle atmospheric water vapour isotopes

A. Zahn¹, P. Franz^{2,3}, C. Bechtel⁴, J.-U. Grooß⁶, and T. Röckmann^{2,5}

¹Institute of Meteorology and Climate Research, Forschungszentrum Karlsruhe, Germany

²Max-Planck-Institute for Nuclear Physics, Heidelberg, Germany

³National Institute for Water and Atmospheric Research (NIWA), Wellington, New Zealand

⁴Robert Bosch GmbH, Buhl, Germany

⁵Institute for Marine and Atmospheric Research Utrecht, Utrecht University, The Netherlands

⁶Institute of Chemistry and Dynamics of the Geosphere, Forschungszentrum Jülich, Germany

Received: 11 June 2003 – Published in Atmos. Chem. Phys. Discuss.: 28 July 2003

Revised: 10 February 2006 – Accepted: 22 April 2006 – Published: 20 June 2006

Abstract. A one-dimensional chemistry model is applied to study the stable hydrogen (D) and stable oxygen isotope (^{17}O , ^{18}O) composition of water vapour in stratosphere and mesosphere. In the troposphere, this isotope composition is determined by “physical” fractionation effects, that are phase changes (e.g. during cloud formation), diffusion processes (e.g. during evaporation from the ocean), and mixing of air masses. Due to these processes water vapour entering the stratosphere first shows isotope depletions in D/H relative to ocean water, which are ~ 5 times of those in $^{18}\text{O}/^{16}\text{O}$, and secondly is mass-dependently fractionated (MDF), i.e. changes in the isotope ratio $^{17}\text{O}/^{16}\text{O}$ are ~ 0.52 times of those of $^{18}\text{O}/^{16}\text{O}$. In contrast, in the stratosphere and mesosphere “chemical” fractionation mechanisms, that are the production of H_2O due to the oxidation of methane, re-cycling of H_2O via the HO_x family, and isotope exchange reactions considerably enhance the isotope ratios in the water vapour imported from the troposphere. The model reasonably predicts overall enhancements of the stable isotope ratios in H_2O by up to $\sim 25\%$ for D/H, $\sim 8.5\%$ for $^{17}\text{O}/^{16}\text{O}$, and $\sim 14\%$ for $^{18}\text{O}/^{16}\text{O}$ in the mesosphere relative to the tropopause values. The $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ ratios in H_2O are shown to be a measure of the relative fractions of HO_x that receive the O atom either from the reservoirs O_2 or O_3 . Throughout the middle atmosphere, MDF O_2 is the major donor of oxygen atoms incorporated in OH and HO_2 and thus in H_2O . In the stratosphere the known mass-independent fractionation (MIF) signal in O_3 is in a first step transferred to the NO_x family and only in a second step to HO_x and H_2O . In contrast to CO_2 , $\text{O}(^1\text{D})$ only plays a minor role in this MIF transfer. The major uncertainty in our calculation arises from poorly quantified isotope exchange reaction rate coefficients and kinetic isotope fractionation factors.

1 Introduction

Water vapour (H_2O) belongs to the most important trace gases in the Earth’s atmosphere. It plays a key role for numerous homogeneous and heterogeneous chemical reactions (Lelieveld and Crutzen, 1990, 1994) as well as for the short-wave and long-wave radiative budget of the atmosphere (IPCC, 2001). Its extremely complex atmospheric cycle is not understood in sufficient detail, in particular since atmospheric water is present in the gaseous, liquid, and solid phase.

The interest in middle atmospheric H_2O was further intensified following observations made by Oltmans and Hofmann (1995) and after this by others (SPARC, 2000, and references therein; Rosenlof et al., 2001) who found increasing H_2O concentrations of $30\text{--}150\text{ nmol/mol yr}^{-1}$ in the middle atmosphere since 1954. Not only the possible causes of this trend but also the consequences for Earth’s climate and the chemistry of the middle atmosphere are a matter of vital discussion (Forster and Shine, 1999, 2002; Kirk-Davidoff et al., 1999; Stenke and Grewe, 2004; Röckmann et al., 2004).

To date primarily H_2O concentration measurements, supported by atmospheric circulation models, have been used to place constraints on the hydrological cycle in the middle atmosphere (Dessler et al., 1995; Rosenlof et al., 1997; Randel et al., 2001). Independent information can be gained from the analysis of the isotopic composition of water vapour.

The isotope ratios in water vapour are usually reported as per mil deviation of the ratio “rare isotopologue” to “most abundant isotopologue” relative to the Vienna Standard Mean Ocean Water (V-SMOW) reference, e.g. $\delta^{18}\text{O}(\text{H}_2\text{O}) = (\text{R}_{18\text{O, sample}}/\text{R}_{18\text{O, V-SMOW}} - 1) \cdot 1000\text{‰}$, where $\text{R}_{18\text{O}}$ denotes the isotopologue ratio $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$ of a sample or V-SMOW, respectively. $\text{R}_{\text{D, V-SMOW}}$ is $0.31152 \cdot 10^{-3}$ (Hagemann et al., 1970; DeWit et al., 1980; Tse et al., 1980), $\text{R}_{17\text{O, V-SMOW}}$ is $0.3799 \cdot 10^{-3}$ (Li et al., 1988), and $\text{R}_{18\text{O, V-SMOW}}$ is $2.0052 \cdot 10^{-3}$ (Baertschi, 1976). All δD ,

Correspondence to: A. Zahn
(andreas.zahn@imk.fzk.de)

$\delta^{17}\text{O}$, and $\delta^{18}\text{O}$ values in this paper are given with respect to V-SMOW.

The major source of atmospheric water vapour is the ocean having an isotope composition close to V-SMOW, i.e., $\delta^{18}\text{O}(\text{H}_2\text{O}) \approx 0\text{‰}$. Evaporation into the atmosphere leads to depletion in the rare H₂O isotopologues relative to H₂¹⁶O, due to their lower vapour pressure compared to H₂¹⁶O, the vapour pressure isotope effect (v.p.i.e.). Typically, $\delta^{18}\text{O}(\text{H}_2\text{O})$ is -12‰ and $\delta\text{D}(\text{H}_2\text{O})$ is -85‰ just above the ocean (Rozanski et al., 1993). Cooling during upward air movement causes cloud formation and (due to the v.p.i.e.) preferential condensation and subsequent removal of the rare H₂O isotopologues by precipitation. The D/H, ¹⁷O/¹⁶O, and ¹⁸O/¹⁶O isotope ratios in H₂O thus decrease with altitude and reach tropopause values in the range of $\delta\text{D}(\text{H}_2\text{O}) \approx -(450\text{--}750)\text{‰}$, $\delta^{17}\text{O}(\text{H}_2\text{O}) \approx -(30\text{--}70)\text{‰}$, and $\delta^{18}\text{O}(\text{H}_2\text{O}) \approx -(60\text{--}130)\text{‰}$, respectively (see Sect. 2). This isotopically depleted water vapour is transported to the stratospheric overworld, almost exclusively within the tropics (Holton et al., 1995; Highwood and Hoskins, 1999).

There and in contrast to the troposphere, chemical reactions considerably modify the isotope composition of the water vapour imported from the troposphere such as: (i) methane (CH₄) oxidation, the main in situ source of H₂O in the stratosphere, (ii) exchange of oxygen atoms with molecular oxygen and ozone via the HO_x and NO_x family, and (iii) oxygen isotope exchange reactions e.g. between H₂O and OH (Greenblatt and Howard, 1988; Masgrau et al., 1999). Importantly, all of these processes enrich the water vapour imported from the troposphere in the rare isotopes.

Using a one-dimensional (1-D) model we show in this paper, how these chemical reactions modify the stable isotope composition of middle atmospheric H₂O and how H₂O isotope observations may be exploited to infer constraints on these reactions and on the budget of stratospheric water. Four previous model studies on the isotopic composition of stratospheric H₂O have been made. Kaye (1990) first studied $\delta^{18}\text{O}(\text{H}_2\text{O})$ in the middle atmosphere and suggested a significant increase in $\delta^{18}\text{O}(\text{H}_2\text{O})$ with altitude due to ¹⁸O-rich excess water from CH₄ oxidation. Ridal et al. (2001) and Ridal (2002) focused on $\delta\text{D}(\text{H}_2\text{O})$ in the stratosphere. They found a strong vertical increase of $\delta\text{D}(\text{H}_2\text{O})$, also due to CH₄ oxidation which is additionally modulated by the seasonally varying H₂O input from the troposphere (the “tape recorder effect”). Johnson et al. (2001a) applied a simple photochemical model with many simplifications, but inferred excellent agreement with own $\delta\text{D}(\text{H}_2\text{O})$ and $\delta^{18}\text{O}(\text{H}_2\text{O})$ balloon-borne observations conducted between 1989 and 1997.

The major difference of the present model study compared to earlier work is first that all three stable isotope signatures $\delta\text{D}(\text{H}_2\text{O})$, $\delta^{17}\text{O}(\text{H}_2\text{O})$, and $\delta^{18}\text{O}(\text{H}_2\text{O})$ both in the stratosphere as well as in the mesosphere are combined, and second that a large number of isotope exchange reactions and all isotope fractionation coefficients measured so far are considered. Special emphasis is put on the specific pathways of D,

¹⁷O, and ¹⁸O from their reservoir species CH₄, H₂, O₂, and O₃ into the end product H₂O.

2 Available stable isotope data of H₂O

Due to the difficulty to measure the isotopic composition of stratospheric water with sufficient accuracy, only a limited number of H₂O isotope data have been gathered so far, which are grouped in the following according to the analytical technique employed.

(i) Most stable isotope H₂O data were collected using remote-sensing infrared spectroscopy techniques (Abbas et al., 1987; Carli and Park, 1988; Guo et al., 1989; Dinelli et al., 1991, 1997; Rinsland et al., 1984, 1991; Stowasser et al., 1999; Johnson et al., 2001; Kuang et al., 2003). They all reveal strong depletions of $\delta\text{D}(\text{H}_2\text{O})$ with respect to V-SMOW which significantly decrease with altitude, from about $-(660 \pm 80)\text{‰}$ at the tropical tropopause (Moyer et al., 1996; Johnson et al., 2001; Kuang et al., 2003; McCarthy et al., 2004) to typically $-(450 \pm 70)\text{‰}$ at 40 km. Observations by Stowasser et al. (1999) showed extreme $\delta\text{D}(\text{H}_2\text{O})$ depletions as low as -830‰ at 17 km inside the Arctic vortex, which was attributed to condensation and subsequent sedimentation of polar stratospheric cloud (PSC) particles.

For $\delta^{17}\text{O}(\text{H}_2\text{O})$ and $\delta^{18}\text{O}(\text{H}_2\text{O})$, most studies report values between 0 and -100‰ and a weak vertical increase. However, this increase is mostly not significant due to the large measurement uncertainties of 50–120‰. In contrast, early observations by Guo et al. (1989) showed increasing $\delta^{18}\text{O}(\text{H}_2\text{O})$ values from $(80 \pm 140)\text{‰}$ at 22 km altitude to $(400 \pm 250)\text{‰}$ at 37 km. Using a balloon-borne spectrometer, Johnson et al. (2001) obtained low isotope ratios of $-(300\text{--}30)\text{‰}$ (average: -128‰) for $\delta^{18}\text{O}(\text{H}_2\text{O})$, and of $-(400\text{--}0)\text{‰}$ (average: -84‰) for $\delta^{17}\text{O}(\text{H}_2\text{O})$ at 12–20 km altitude.

(ii) Cryogenic in situ sampling and subsequent laboratory-based mass spectrometry (MS) analysis constitutes the potentially most accurate technique, but suffers from the very small sample amounts available and their difficult handling and MS analysis. Most observations are from the upper troposphere and lowermost stratosphere (Ehnhalt, 1974; Smith, 1992; Zahn et al., 1998; Zahn, 2001) and to date there is only one set of balloon-borne stratospheric $\delta\text{D}(\text{H}_2\text{O})$ profiles available (Pollock et al., 1980). These data likewise show a continuous increase in $\delta\text{D}(\text{H}_2\text{O})$ with altitude, from about -450‰ at 25 km to about -360‰ at 35 km.

The single investigation on the oxygen ($\delta^{17}\text{O}$ and $\delta^{18}\text{O}$) isotope composition of stratospheric H₂O samples was conducted by Franz and Röckmann (2005) using samples obtained between New Zealand and Antarctica in August/October 2004 at altitudes of up to ~ 5 km above the local tropopause. The data show an increase of $\delta^{18}\text{O}$ concomitant with decreasing H₂O mixing ratios above the local tropopause. This was interpreted as mixing of tropospheric and stratospheric overworld air in the high latitude

lowermost stratosphere. Notably, the data show no oxygen isotope anomaly with very small errors of $\Delta^{17}\text{O}(\text{H}_2\text{O}) < 2\text{‰}$.

(iii) In situ infrared laser spectroscopic techniques are challenging, potentially very accurate and may additionally offer high spatial resolution. First applications on board aircraft have been reported.

Using the tunable diode laser absorption spectrometer (TDLAS) ALIAS on board the high-flying NASA WB-57 aircraft, Webster and Heymsfield (2003) observed (expectedly) decreasing δD , $\delta^{17}\text{O}$, and $\delta^{18}\text{O}$ values in H₂O with increasing height up to the tropical tropopause. The high temporal resolution measurement also revealed a very high degree of variability, e.g. δD values ranging from 0 and -900‰ near the tropopause and clearly different values for ice and gas water, respectively. Surprisingly, the mean $\delta\text{D}:\delta^{18}\text{O}$ ratio for this data set is only <3 in the lower stratosphere.

In May 2004 Kerstel, Romanini, and Jost applied a cavity-ring-down technique (off-axis cavity enhanced absorption spectroscopy, OF-CEAS) on-board a DC-10 aircraft at altitudes of up to 13 km. They reported on excellent measurement uncertainties of below 10‰ for all three stable isotopologues over a certain 10 min sampling interval with particular constant H₂O mixing ratios of ~ 200 ppmv (personal communication).

High measurement accuracies are reported by Keutsch et al. (Harvard University) who measured δD and $\delta^{18}\text{O}$ in H₂O at altitudes of up to 20 km in autumn 2004 by using off-axis integrated cavity output spectroscopy (OF-ICOS) on-board the NASA WB-57. On the same flights a photofragment laser-induced fluorescence (LIF) technique were applied for measuring δD in H₂O by Hanisco et al. (Harvard University) with similarly low measurement uncertainty.

3 Information provided by the H₂O isotopic composition

The isotopic composition of tropospheric water vapour is controlled by the hydrological cycle. Hence, H₂O isotope data can be used as tracers for the condensation history of probed air masses (Taylor, 1984), e.g. for studying the transport of tropospheric H₂O into the lowermost stratosphere (Zahn, 2001).

Both, $\delta\text{D}(\text{H}_2\text{O})$ and $\delta^{18}\text{O}(\text{H}_2\text{O})$ are primarily determined by the v.p.i.e. (see Sect. 1) and thus undergo similar variations. Indeed, in surface precipitation both isotopologues are closely related by the meteoric water line (MWL): $\delta\text{D}(\text{H}_2\text{O}) \approx m \times \delta^{18}\text{O}(\text{H}_2\text{O}) + 10\text{‰}$, with $m \approx 8$ (Craig, 1961). This relationship was found to hold reasonably well even on Mount Logan (Canada) at 5951 m altitude, with $m = 7.5$ (Holdsworth et al., 1991). At cold temperatures as encountered in the tropical tropopause layer (TTL), however, kinetic isotope fractionation during formation of ice cloud particles, their lofting in convective cells and mixing of air masses with different H₂O isotope compositions are assumed to consid-

erably reduce $\delta\text{D}(\text{H}_2\text{O})$ depletion compared to $\delta^{18}\text{O}(\text{H}_2\text{O})$ (Moyer et al., 1996; Keith, 2000; Johnson et al., 2001; Kuang et al., 2003; Dessler and Sherwood, 2003). In fact, using the isotope composition of water vapour entering the stratosphere of $\delta\text{D}(\text{H}_2\text{O}) = -679\text{‰}$ and $\delta^{18}\text{O}(\text{H}_2\text{O}) = -128\text{‰}$ as measured by Johnson et al. (2001), a mean slope $m = 5.4$ is calculated. Due to the mass-dependent nature of isotope fractionation processes in the troposphere, $\Delta^{17}\text{O}(\text{H}_2\text{O})$ is set to 0‰ at the tropical tropopause. Potential deviations from this assumption e.g. owing to an interplay of equilibrium and kinetic isotope fractionation factors with different three-isotope relationships (Eq. 1) were not observed yet and thus are not considered.

In this paper, we define mass-independent fraction (MIF) by using the formulation

$$\Delta^{17}\text{O} = [\ln(1 + \delta^{17}\text{O}/1000) - \lambda \cdot \ln(1 + \delta^{18}\text{O}/1000)] \cdot 1000\text{‰} \quad (1)$$

suggested by Miller (2002) which quantifies the deviation from mass-dependent fractionation without approximation. As three isotope exponent we adopt $\lambda = 0.528 (\pm 0.0015)$ as measured by Meijer and Li (1998) in a large number of natural waters showing $\delta^{18}\text{O}(\text{H}_2\text{O})$ values between -50 and $+10\text{‰}$. This value is very close to $\lambda = 0.529$ derived by Young et al. (2002) for equilibrium fractionation processes, but larger than $\lambda = 0.513$ inferred for kinetic fractionation processes. It is not known to date, if kinetic fractionation during the upward transport to the tropopause results in significantly lower λ values for H₂O at the tropopause. Assuming $\delta^{18}\text{O}(\text{H}_2\text{O}) = -128\text{‰}$ at the tropical tropopause and $\lambda = 0.513$ (which is also the λ value for O₂), Eq. (1) leads to only 2.05‰ lower $\delta^{17}\text{O}(\text{H}_2\text{O})$ values. This in an exaggerated upper limit, since λ is certainly not that different for the entire condensation history. In any case, such a shift would not alter much our model results.

In conclusion, it can be presumed that tropospheric water vapour entering the stratosphere at the tropical tropopause on average exhibits a $\delta\text{D}(\text{H}_2\text{O})/\delta^{18}\text{O}(\text{H}_2\text{O})$ ratio of 5–6 and is mass-dependently fractionated (MDF). Possible local deviations from these two assumptions, e.g. assumed to occur in the outflow of a deep convection cells will be negligible for the H₂O isotope budget and are not considered here.

In the stratosphere chemical reactions modify this isotope signature imported from the troposphere, as will be pointed out briefly below and explained in more detail later:

(i) The first “chemical” mechanism is the in-situ source of H₂O, the oxidation of methane (and H₂). Methane is oxidized in the middle atmosphere by reactions with OH, Cl, and O(¹D), and by photolysis (Lary and Toumi, 1997). Each oxidized CH₄ molecule leads to the net formation of almost two H₂O molecules (Evans et al., 1999; Zöger et al., 1999; Michelsen et al., 2000). The δD value of the produced H₂O molecule $\delta\text{D}(\text{H}_2\text{O})$ differs from $\delta\text{D}(\text{CH}_4)$, because the CH₄ loss reactions are accompanied by unusually strong kinetic isotope fractionation. For instance, at room temperature the D isotope fractionation factor KIE^{D} , that is the ratio of the

rate constants $k(\text{CH}_4)/k(\text{CH}_3\text{D})$, is $\text{KIE}^{\text{D}}(\text{OH})=1.29$ for the reaction of CH₄ with OH, $\text{KIE}^{\text{D}}(\text{Cl})=1.51$ for the reaction with Cl, and $\text{KIE}^{\text{D}}(\text{O}^{18}\text{D})=1.11$ for the reaction with O(¹D) (Saueressig et al., 1996, 2001; Tyler et al., 2000). Since these KIEs differ considerably, the $\delta\text{D}(\text{H}_2\text{O})$ distribution in the middle atmosphere is expected to be determined by the partitioning of the different CH₄ oxidation reactions.

(ii) Re-cycling of oxygen atoms between H₂O and the oxygen reservoir gases O₂ and O₃ via HO_x and NO_x species and oxygen isotope exchange reactions. Besides net H₂O formation due to CH₄ oxidation, continuous loss of H₂O and reformation of H₂O lead to an extensive turnover of oxygen atoms between oxygen containing trace gases. This process recycles much more H₂O molecules than are net produced by the oxidation of CH₄ (see Fig. 5). Though a zero-cycle with respect to the H₂O mass, it strongly influences the oxygen isotope composition of H₂O. This process is expected to dominate the MIF oxygen isotope signal from O₃ to H₂O. Further processes to be considered are a few oxygen isotope exchange reactions such as between OH and H₂O and NO₂ and H₂O.

A crucial and exciting point is that more than 99% of all oxygen atoms that end up in H₂O in the middle atmosphere stem from the hydroxyl radical OH. Hence, $\delta^{17}\text{O}(\text{H}_2\text{O})$ and $\delta^{18}\text{O}(\text{H}_2\text{O})$ data provide information about the oxygen isotope composition of OH, and by considering $\Delta^{17}\text{O}(\text{H}_2\text{O})$ about the affection of MIF enriched O₃ upon OH_x and via OH_x upon many other oxygen containing trace gases in the middle atmosphere. This MIF transfer from O₃ to oxygen-containing radicals was first studied by Lyons (2001).

4 Model description

Our 1-D model encompasses 65 boxes from 15 to 80 km, each 1 km high. Temperature and pressure profiles are set according to the U.S. Standard Atmosphere (1976). Vertical transport is parameterised by eddy diffusion coefficients K_z , below 29 km using the “National Academy of Science (1976)” profile, from 29 km to 50 km using the “Hunten” profile, both depicted by Massie and Hunten (1981), and above 50 km employing the profile given by Froidevaux and Yung (1982).

4.1 Peculiarities in modelling isotope ratios

The concept of chemical families frequently applied in atmospheric chemistry models mostly fails if isotopologues are considered. For instance, the reaction chain of $\text{CO}+\text{OH}\rightarrow\text{CO}_2+\text{H}$ followed by $\text{H}+\text{O}_2+\text{M}\rightarrow\text{HO}_2+\text{M}$ converts OH to HO₂, which conserves the sum of $\text{HO}_x=\text{OH}+\text{HO}_2$. The oxygen atom of the initial OH, however, is incorporated in CO₂ and thus leaves the HO_x family. A new OH bond is formed, which has the oxygen isotope composition of O₂.

The following peculiarities also have to be taken into account:

- (i) Kinetic isotope fractionation factors that account for the mostly slower reaction rate of the isotopically substituted molecule compared to the most abundant isotopologue.
- (ii) Isotope exchange reactions such as the fast O exchange between O₂ and O(³P) (Kaye and Strobel, 1983). They modify isotope ratios but not the concentration of the participating compounds.
- (iii) When including isotopologues and isotopomers that contain two or more atoms of the same element at non-equivalent positions such as O₃ or HO₂, the individual isotopomers have to be considered separately, e.g. the OQO and OOQ or HQO and HOQ (with Q substituting for ¹⁷O and ¹⁸O).

4.2 Trace gas chemistry

Due to negligible cloud formation in the middle atmosphere, our model is restricted to gas phase chemistry. If not cited differently, all reaction rates are taken from JPL (2003). Initially, all reactions involved in H₂O chemistry and isotope exchange with other gases were assessed carefully for all altitudes covered by the model. The reactions finally used (Tables 1 and 2) always account for more than 95% of the local chemical turnover of H₂O and its isotopologues at a given altitude.

Water vapour is formed due to H-abstraction by OH, i.e. $\text{XH}_i+\text{OH}\rightarrow\text{XH}_{i-1}+\text{H}_2\text{O}$, where XH_i is CH₄ (Reaction R1), CH₂O (R8), HO₂ (R16), HCl (R21), H₂ (R26), or HNO₃ (R29). The major sinks of middle atmospheric H₂O are the reaction with O(¹D) (R30) and photolysis at wavelength below 200 nm (R31).

Furthermore, all reactions that are necessary to maintain the overall budget of O- and H-atoms balanced are included. To this end a complete methane destruction scheme (LeTexier et al., 1988) and all relevant reactions affecting the HO_x-family (Burnett and Burnett, 1995) are considered.

The concentrations and the isotopic compositions of H₂O, OH, HO₂, H, H₂, CH₄, CH₃, CH₂O, HCO, HNO₃, and HCl are explicitly calculated by the model.

4.3 Isotope chemistry

Integration of isotopologues renders the model complex, as shown for the initial steps of the major methane destruction reactions (Table 3).

Only for a few of the reactions listed in Table 1 the isotope fractionation factor $\text{KIE}=k/k'$ is known, with k' being the rate constant for the isotopically substituted species. All KIEs that have been measured in the laboratory are implemented in the model (Table 5), expressed in the form:

$$\text{KIE} = A \cdot \exp(E/T) \quad (2)$$

Table 1. Considered gas phase reactions.

No	reaction	rate ^a		br, n ^b
		A	E	
(R1)	CH ₄ +OH→CH ₃ +H ₂ O		Table 3	
(R2)	CH ₄ +O(¹ D)→...		Table 3	
(R3)	CH ₄ +Cl→CH ₃ +HCl		Table 3	
(R4)	CH ₄ +γ→CH ₃ +H		Table 3	
(R5)	CH ₃ +O ₂ +M→CH ₃ O ₂ +M		Table 2	
(R6)	CH ₃ O ₂ +NO→CH ₃ O+NO ₂	2.8(−12)	−300	
(R7)	CH ₃ O+O ₂ →CH ₂ O+HO ₂	3.9(−14)	900	
(R8)	CH ₂ O+OH→CHO+H ₂ O	1.0(−11)	0	
(R9)	CH ₂ O+γ→CHO+H/CO+H ₂		altitude dependent	
(R10)	CH ₂ O+O(³ P)→CHO+OH	3.4(−10)	1600	
(R11)	CH ₂ O+Cl→CHO+HCl	8.1(−11)	30	
(R12)	HCO+O ₂ →CO+HO ₂	3.5(−12)	−140	
(R13)	H+O ₂ +M→HO ₂ +M		Table 2	
(R14)	H+O ₃ →OH+O ₂	1.4(−10)	470	
(R15) ^a	H+HO ₂ →2OH	8.1(−11)	0	0.87
(R15) ^b	H+HO ₂ →H ₂ O+O ₂	8.1(−11)	0	0.09
(R15) ^c	H+HO ₂ →H ₂ O+O(³ P)	8.1(−11)	0	0.02
(R16)	OH+HO ₂ →H ₂ O+O ₂	4.8(−11)	−250	
(R17)	OH+O ₃ →HO ₂ +O ₂	1.6(−12)	940	
(R18)	OH+O(³ P)→H+O ₂	2.2(−11)	−120	
(R19)	OH+OH→H ₂ O+O(³ P)	4.2(−12)	240	
(R20)	OH+NO ₂ +M→HNO ₃ +M		Table 2	
(R21)	HCl+OH→H ₂ O+Cl	2.6(−12)	350	
(R22)	CO+OH→CO ₂ +H	1.5(−13)	0	
(R23)	HO ₂ +NO→OH+NO ₂	3.5(−12)	−250	
(R24)	HO ₂ +O(³ P)→OH+O ₂	3.0(−11)	−200	
(R25)	HO ₂ +O ₃ →OH+2·O ₂	1.1(−14)	500	
(R26)	H ₂ +OH→H ₂ O+H	5.5(−12)	2000	
(R27)	H ₂ +O(¹ D)→H+OH	1.1(−10)	0	
(R28)	H ₂ +Cl→H+HCl	3.7(−11)	2300	
(R29)	HNO ₃ +OH→H ₂ O+NO ₃			
(R30)	H ₂ O+O(¹ D)→2·OH	2.2(−10)	0	
(R31) ^a	H ₂ O+γ→H+OH, γ=121.6 nm	5.25(−6)	−4.4(−19)	0.917
(R31) ^b	H ₂ O+γ→H+OH, γ>130 nm	1.20(−6)	−1.0(−7)	0.35

^a rate constant $k(T)=A \cdot \exp[-(E \cdot K/T)]$ in cm³ s^{−1}

photolysis rate $j(z)=A \cdot \exp[E \cdot L(z)^n]$ in s^{−1}, with $L(z)$: number of molecules cm^{−2} above altitude z .

^b br: branching rate, n: exponent in $j(z)$

For some KIEs no temperature dependence is known and thus is set constant. For the reactions for which the KIE has not been explicitly measured, KIE is set to $(\mu'/\mu)^{1/2}$, with $\mu=m_1 \cdot m_2/(m_1+m_2)$ being the reduced mass of the reactants of mass m_1 and m_2 . This accounts for the fact that the rate constant of a certain reaction does not only depend on the reactivity of the reactants, but also on their collision frequency and thus thermal speed.

Additionally, the known oxygen exchange reactions were included (Table 5).

4.4 Trace gas parameter profiles

Fixed, globally, seasonally and diurnally averaged profiles are used for the trace gases O₃, O(¹D), NO, NO₂, and Cl. These were derived from a simulation of the Mainz photochemical 2-D model (Groß, 1996), as an annually and diurnally averaged profile of the HNO₃ photolysis frequency.

Table 2. Termolecular reactions.

No.	Reaction	k_0^{300} a	n	k_∞^{300} b	m
(5)	$\text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{M}$	4.5×10^{-31}	3.0	1.8×10^{-12}	1.7
(13)	$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$	5.7×10^{-32}	1.6	7.5×10^{-11}	0.0
(20)	$\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$	2.5×10^{-30}	4.4	1.6×10^{-11}	1.7

$$^a k_0(T) = k_0^{300} \cdot \left(\frac{T}{300}\right)^{-n}$$

$$^b k_\infty(T) = k_\infty^{300} \cdot \left(\frac{T}{300}\right)^{-m}$$

$$\text{rate constant } k(M, T) = \left(\frac{k_0(T)[M]}{1 + (k_0(T)[M]/k_\infty(T))} \right) \cdot 0.6^{(1 + [\log_{10}(k_0(T)[M]/k_\infty(T))]^2)^{-1}}$$

[M] being the number concentrations of air molecules and T the temperature.

Table 3. Detailed description of the initial methane destruction reactions.

No	reaction	rate		branching ratio	fractionation factor
		A	E		
(1)	$\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$	2.45 (−12)	1775	1	1
	$\text{CH}_4 + {}^{17}\text{OH} \rightarrow \text{CH}_3 + \text{H}_2 {}^{17}\text{O}$	2.45 (−12)	1775	1	0.986
	$\text{CH}_4 + {}^{18}\text{OH} \rightarrow \text{CH}_3 + \text{H}_2 {}^{18}\text{O}$	2.45 (−12)	1775	1	0.973
	$\text{CH}_4 + \text{OD} \rightarrow \text{CH}_3 + \text{HDO}$	2.45 (−12)	1775	1	Table 4
	$\text{CH}_3\text{D} + \text{OH} \rightarrow \text{CH}_2\text{D} + \text{H}_2\text{O}$	3.5 (−12)	1950	0.75	0.985
	$\text{CH}_3\text{D} + \text{OH} \rightarrow \text{CH}_3 + \text{HDO}$	3.5 (−12)	1950	0.25	0.985
	$\text{CH}_3\text{D} + \text{OD} \rightarrow \text{CH}_2\text{D} + \text{HDO}$	3.5 (−12)	1950	0.75	0.971
	$\text{CH}_3\text{D} + \text{OD} \rightarrow \text{CH}_3 + \text{D}_2\text{O}$	3.5 (−12)	1950	0.25	0.971
(2)	$\text{CH}_4 + \text{O}({}^1\text{D}) \rightarrow \text{CH}_3 + \text{OH}$	1.5 (−10)	0	0.75	1
	$\text{CH}_4 + {}^{17}\text{O}({}^1\text{D}) \rightarrow \text{CH}_3 + {}^{17}\text{OH}$	1.5 (−10)	0	0.75	0.985
	$\text{CH}_4 + {}^{18}\text{O}({}^1\text{D}) \rightarrow \text{CH}_3 + {}^{18}\text{OH}$	1.5 (−10)	0	0.75	0.972
	$\text{CH}_4 + \text{O}({}^1\text{D}) \rightarrow \text{CH}_3\text{O} + \text{H}$	1.5 (−10)	0	0.20	1
	$\text{CH}_4 + {}^{17}\text{O}({}^1\text{D}) \rightarrow \text{CH}_3 {}^{17}\text{O} + \text{H}$	1.5 (−10)	0	0.20	0.985
	$\text{CH}_4 + {}^{18}\text{O}({}^1\text{D}) \rightarrow \text{CH}_3 {}^{18}\text{O} + \text{H}$	1.5 (−10)	0	0.20	0.972
	$\text{CH}_4 + \text{O}({}^1\text{D}) \rightarrow \text{CH}_2\text{O} + \text{H}_2$	1.5 (−10)	0	0.05	1
	$\text{CH}_4 + {}^{17}\text{O}({}^1\text{D}) \rightarrow \text{CH}_2 {}^{17}\text{O} + \text{H}_2$	1.5 (−10)	0	0.05	0.985
	$\text{CH}_4 + {}^{18}\text{O}({}^1\text{D}) \rightarrow \text{CH}_2 {}^{18}\text{O} + \text{H}_2$	1.5 (−10)	0	0.05	0.972
	$\text{CH}_3\text{D} + \text{O}({}^1\text{D}) \rightarrow \text{CH}_3 + \text{OD}$	1.5 (−10)	0	0.75-0.70	Table 4
	$\text{CH}_3\text{D} + \text{O}({}^1\text{D}) \rightarrow \text{CH}_2\text{D} + \text{OH}$	1.5 (−10)	0	0.25-0.70	Table 4
	$\text{CH}_3\text{D} + \text{O}({}^1\text{D}) \rightarrow \text{CH}_2\text{DO} + \text{H}$	1.5 (−10)	0	0.75-0.20	Table 4
	$\text{CH}_3\text{D} + \text{O}({}^1\text{D}) \rightarrow \text{CH}_3\text{O} + \text{D}$	1.5 (−10)	0	0.25-0.20	Table 4
	$\text{CH}_3\text{D} + \text{O}({}^1\text{D}) \rightarrow \text{CHDO} + \text{H}_2$	1.5 (−10)	0	0.75-0.05	Table 4
	$\text{CH}_3\text{D} + \text{O}({}^1\text{D}) \rightarrow \text{CH}_2\text{O} + \text{HD}$	1.5 (−10)	0	0.25-0.05	Table 4
(3)	$\text{CH}_4 + \text{Cl} \rightarrow \text{CH}_3 + \text{HCl}$	1.1 (−11)	1400	1	1
	$\text{CH}_3\text{D} + \text{Cl} \rightarrow \text{CH}_3 + \text{DCl}$	1.1 (−11)	1400	0.25	Table 4
	$\text{CH}_3\text{D} + \text{Cl} \rightarrow \text{CH}_2\text{D} + \text{HCl}$	1.1 (−11)	1400	0.75	Table 4
(4)	$\text{CH}_4 + \gamma \rightarrow \text{CH}_3 + \text{H}$	5.5 (−6)	−4.4(−19)	1	$n=0.917^a$
	$\text{CH}_3\text{D} + \gamma \rightarrow \text{CH}_3 + \text{D}$	5.5 (−6)	−4.4(−19)	0.25	$n=0.917^a$
	$\text{CH}_3\text{D} + \gamma \rightarrow \text{CH}_2\text{D} + \text{H}$	5.5 (−6)	−4.4(−19)	0.75	$n=0.917^a$

^a Brasseur and Solomon (1986), with photolysis rate $j(z) = A \cdot \exp[E \cdot L(z)^n]$ in s^{-1} , $L(z)$ being the number of molecules per cm^2 above altitude z .

4.5 Isotope parameter profiles of O(³P), O₃, O(¹D), and NO

The oxygen isotope compositions assumed for O₂, O(³P), O₃, and O(¹D) are indicated in Fig. 1 together with the calculated isotope profiles for NO, OH, and HO₂.

The isotope composition of

(i) O₂ is $\delta^{17}\text{O}(\text{O}_2) = 11.78\text{‰}$ and $\delta^{18}\text{O}(\text{O}_2) = 22.96\text{‰}$ (Luz et al., 1999; Coplen et al., 2002),

(ii) O(³P) is controlled by the rapid exchange reaction with O₂ (Kaye and Strobel, 1983), which shows significant

Table 4. Considered fractionation factors, defined as $\text{KIE}(T) = \text{KIE}(0) \cdot \exp(B/T)$.

No	reaction	KIE(0)	B ^a	KIE(300K)	reference
(1)	$\text{CH}_3\text{D} + \text{OH} \rightarrow \text{CH}_2\text{D} + \text{H}_2\text{O}$	0.605	215.00	1.239	Gierczak et al. (1997)
(1)	$\text{CH}_4 + \text{OD} \rightarrow \text{CH}_3 + \text{HDO}$	1.120	−55.00	0.932	Gierczak et al. (1997)
(2)	$\text{CH}_3\text{D} + \text{O}(^1\text{D}) \rightarrow \text{CH}_3 + \text{OD}$	1.060	0.00	1.060	Saueressig et al. (2001)
(3)	$\text{CH}_3\text{D} + \text{Cl} \rightarrow \text{CH}_3 + \text{DCI}$	1.278	51.31	1.516	Saueressig et al. (1996)
(8)	$\text{CHDO} + \text{OH} \rightarrow \text{HCO} + \text{HDO}$	0.7812	0.00	0.781	Feilberg et al. (2004)
(8)	$\text{CH}_2\text{Q} + \text{OH} \rightarrow \text{HCO} + \text{H}_2\text{Q}$	1.0341	0.00	1.034	Feilberg et al. (2004)
(11)	$\text{CHDO} + \text{Cl} \rightarrow \text{HCO} + \text{DCI}$	0.8326	0.00	0.833	Feilberg et al. (2004)
(11)	$\text{CH}_2\text{Q} + \text{Cl} \rightarrow \text{HCQ} + \text{DCI}$	0.9259	0.00	0.926	Feilberg et al. (2004)
(26)	$\text{HD} + \text{OH} \rightarrow \text{HDO} + \text{H}$	1.100	130.00	1.697	JPL (2003)
(27)	$\text{HD} + \text{O}(^1\text{D}) \rightarrow \text{H} + \text{OD}$	1.130	0.00	1.130	Talukdar and Ravishankara (1996)

^a if B = 0, no temperature dependency has been measured so far.

Table 5. Considered oxygen isotope exchange reactions.

No	reaction	Rate		reference
		A	E	
(32)	$\text{QH} + \text{NO} \rightleftharpoons \text{OH} + \text{NQ}$	1.8(−11)	0	Dubey et al. (1997)
(33)	$\text{QH} + \text{NO}_2 \rightleftharpoons \text{OH} + \text{NOQ}$	1.0(−11)	0	Greenblatt and Howard (1989)
(34)	$\text{QH} + \text{H}_2\text{O} \rightleftharpoons \text{OH} + \text{H}_2\text{Q}$	1.6(−13)	2100	Greenblatt and Howard (1989)
(35)	$\text{HOQ} + \text{OH} \rightleftharpoons \text{HO}_2 + \text{QH}$	1.7(−11)	−400	Dransfeld and Wagner (1987)
(36)	$\text{Q} + \text{O}_2 \rightleftharpoons \text{OQ} + \text{O}$			see Sect. 4.5
(37)	$\text{Q} + \text{NO} \rightleftharpoons \text{O} + \text{NQ}$			see Sect. 4.5
(38)	$\text{NOQ} + \text{H}_2\text{O} \rightleftharpoons \text{NO}_2 + \text{H}_2\text{Q}$	2.3(−13)	2100	Jaffe and Klein (1966)
(39)	$\text{QH} + \text{O}_2 \rightleftharpoons \text{OH} + \text{OQ}$	<1(−17)	0	Greenblatt and Howard (1989)
(40)	$\text{HOQ} + \text{O}_2 \rightleftharpoons \text{HO}_2 + \text{OQ}$	<3(−17)	0	Sinha et al. (1987)
(41)	$\text{NOQ} + \text{O}_2 \rightleftharpoons \text{NO}_2 + \text{OQ}$	<1(−24)	0	Sharma et al. (1970)

fractionation and leads to $\delta^{17}\text{O}(\text{O}(^3\text{P})) = -27.58\text{‰}$ and $\delta^{18}\text{O}(\text{O}(^3\text{P})) = -55.30\text{‰}$ (Johnston et al., 2000).

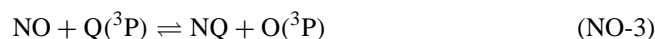
(iii) O₃ was set to be solely dependent on temperature, because all laboratory data indicate negligible pressure dependence below 100 hPa and because it appears that all reliable atmospheric data agree with the enrichments determined in laboratory studies (Johnson et al., 2000; Mauersberger et al., 2001). The (consistent) laboratory data by Thieme and Jackson (1988, 1990), Morton et al. (1990), and (Günther et al., 1999) are implemented under the assumption that 80% of the isotope enrichment of O₃ is carried by the asymmetric QOO (Anderson et al., 1989; Janssen et al., 1999; Mauersberger et al., 1999).

Q(¹D) is derived from the isotope enrichment in O₃ under the following further assumptions: (i) during the photolysis of O₃ only the terminal oxygen atoms form O(¹D), (ii) there is negligible fractionation during the photolysis of O₃ (Wen and Thieme, 1993), and (iii) mass-dependent collision rates during subsequent quenching of O(¹D) on N₂ and O₂ to the ground state O(³P) lead to additional isotope enrichment of 19‰ for $\delta^{17}\text{O}$ and 36‰ for $\delta^{18}\text{O}$ in O(¹D) (calculated by using the formula given in Sect. 4.3).

The oxygen isotope composition of middle atmospheric NO_x is not controlled by its main source, i.e. oxidation of N₂O by O(¹D), but by O exchange between O_x and NO_x:



and the fast O-exchange reactions:



Indeed, because of the rapid photochemical cycling less than 0.5% of all O atoms in NO stem from the oxidation of N₂O by O(¹D) over the entire altitude range considered. Hence, the isotopic composition of N₂O that is known to carry a small degree of MIF into the stratosphere (Cliff and Thieme, 1997; Cliff et al., 1999; Röckmann et al., 2001a; Röckmann et al., 2001b; Kaiser and Röckmann, 2005) does not need to be considered. Using a sub-model, the O isotope ($\delta^{17}\text{O}$, $\delta^{18}\text{O}$) parameter profile of NO is derived by calculating the source partitioning of the reactions NO-1 to NO-4. The inferred enrichments in NO and NO₂ (Fig. 1) in the

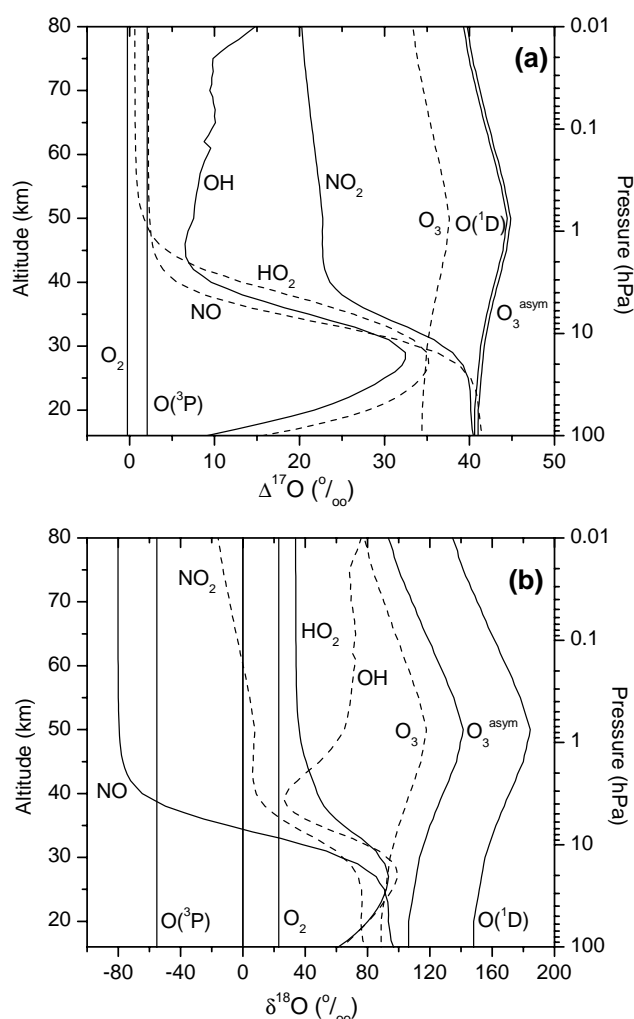


Fig. 1. Vertical profile of $\Delta^{17}\text{O}$ (graph a) and $\delta^{18}\text{O}$ (graph b) assumed for O_2 , $\text{O}(^3\text{P})$, O_3 , asymmetric O_3 , and $\text{O}(^1\text{D})$, and calculated for NO , OH and HO_2 (without considering the isotope exchange reactions R39 and R40).

lower stratosphere (which is due to the O exchange with O_3 , reactions NO-1 and NO-2) is only about half the ones calculated by Lyons (2001), explanation in Sect. 7. Because of the dominance of NO-3, the oxygen isotopic composition of NO in the mesosphere is similar to the one of $\text{O}(^3\text{P})$.

4.6 Boundary conditions

At the lower model boundary, i.e. the tropopause, fixed trace gas and isotope mixing ratios are set as follows: $[\text{H}_2\text{O}] = 3.70 \mu\text{mol/mol}$. $\delta\text{D}(\text{H}_2\text{O}) = -660\text{‰}$ and $\delta^{18}\text{O}(\text{H}_2\text{O}) = -128\text{‰}$ (Moyer et al., 1996; Johnson et al., 2001, 2004; Kuang et al., 2003; McCarthy et al., 2004). $\Delta^{17}\text{O}(\text{H}_2\text{O})$ is set to 0‰ (as no process is known in the troposphere, which could cause MIF in H_2O), so that $\delta^{17}\text{O}(\text{H}_2\text{O})$ is -69.76‰ (in agreement with $-(84 \pm 31)\text{‰}$ observed by Johnson et al., 2001). $[\text{CH}_4] = 1.70 \mu\text{mol/mol}$.

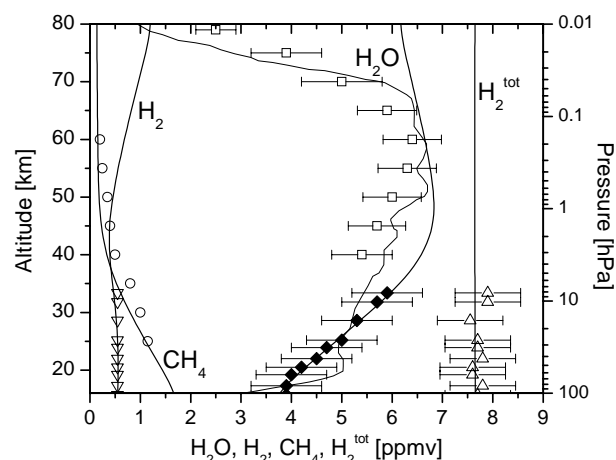


Fig. 2. Calculated vertical profiles of H_2O , CH_4 , H_2 , and H_2^{tot} compared to measurements of H_2O : balloon-borne in situ Lyman- α hygrometer data at 43°N (black diamonds) (Zöger et al., 1999), ATMOS data (light squares) (Michelsen et al., 2002), and HALOE data (line) (Nedoluha et al., 1998); CH_4 , H_2 : cryogenic collection and subsequent laboratory analysis at 43°N (Zöger et al., 1999), and H_2^{tot} : (Zöger et al., 1999).

$\delta\text{D}(\text{CH}_4) = -86\text{‰}$ (Quay et al., 1999). $[\text{H}_2] = 0.55 \mu\text{mol/mol}$ (Zöger et al., 1999). $\delta\text{D}(\text{H}_2) = 130\text{‰}$ (Friedman and Scholz, 1974; Rahn et al., 2003; Rhee et al., 2006). The flux of all considered species across the upper boundary (80 km) is set to zero.

5 Model results and comparison with observations

The model results presented in this section constitute the “base run” where the badly quantified isotope exchange reactions (R38) to (R41) (Table 5) are omitted. The influence of these badly quantified reactions is assessed in Sect. 6.5.

5.1 Vertical trace gas profiles

In Fig. 2 calculated vertical profiles for H_2O , CH_4 , H_2 and the total hydrogen H_2^{tot} are compared with observations. The agreement is good. The difference above 70 km is due to the known strong seasonal variation in this altitude range. For instance, H_2 is expected to vary between 1 ppmv in July and nearly 3 ppmv in January at 70 km altitude (LeTexier et al., 1988).

The destruction of methane in the stratosphere leads to a relevant increase in water vapour. Maximum mixing ratios of 6.5 ppmv are observed at the stratopause. Above 50 km, increasing loss of H_2O due to reaction with OH and above 65 km due to photolysis overcompensates H_2O formation and causes a decline in H_2O and an increase in H_2 . The total hydrogen H_2^{tot} stays constant in the middle atmosphere. The weak decrease in the mesosphere comes along with increasing concentrations of atomic hydrogen H.

5.2 Vertical profiles of $\delta D(H_2O)$, $\delta D(CH_4)$, and $\delta D(H_2)$

The calculated profiles of δD in H₂O, CH₄, and H₂ likewise compare well with observations and the model results obtained by Ridal (2002) for $\delta D(H_2O)$ (Fig. 3).

Apart from the Arctic profile retrieved by (Stowasser et al., 1999), all available $\delta D(H_2O)$ observations (Sect. 2) (although somewhat differing in absolute concentrations) show a vertical increase by $\sim(150\text{--}200)\text{‰}$ between 20 and 40 km. This vertical $\delta D(H_2O)$ increase is due to the increasing fraction of H₂O that originates from the oxidation of CH₄ (see Sect. 3). The $\delta D(H_2O)$ value in the mesosphere, which is higher than the tropopause value by $\sim 250\text{‰}$, suggests that $\sim 60\%$ of the mesospheric H₂O originate from the troposphere and $\sim 40\%$ stem from the oxidation of CH₄ (see Sect. 6.3).

The δD profiles of CH₄ and H₂ agree well with in-situ sampling and subsequent mass-spectrometric laboratory measurements by Röckmann et al. (2003) and Brass et al. (MPI-K Heidelberg, personal communication).

5.3 Vertical Profiles of $\delta^{17}O(H_2O)$ and $\delta^{18}O(H_2O)$

The oxygen isotope ratios in H₂O (Fig. 4) exhibit a vertical profile that is qualitatively similar to that of $\delta D(H_2O)$. However, for the O isotopologues in addition to new H₂O formation photochemical recycling, that is exchange of oxygen isotopes with O₂ and O₃ via HO_x- and NO_x-species, causes additional intensive turnover of $\delta^{17}O(H_2O)$ and $\delta^{18}O(H_2O)$. As a consequence, the relative enrichments are even stronger than for δD , and positive values for $\delta^{17}O$ and $\delta^{18}O$ are reached. Note that both recycled H₂O and newly formed H₂O have the same O isotope signature since both are produced mainly via HO_x (see Sect. 6.4).

The measurements by Dinelli et al. (1991), Guo et al. (1989), Rinsland et al. (1991), and Johnson et al. (2001) are in reasonable agreement with our model results. Consider however the large measurement errors of $\pm(50\text{--}120)\text{‰}$ which is in the same magnitude as the calculated total vertical increase by 85‰ for $\delta^{17}O(H_2O)$ and 150‰ for $\delta^{18}O(H_2O)$.

6 Discussion

6.1 The budget of middle atmospheric water vapour

Figure 5 exhibits the turnover rates of water vapour in the middle atmosphere. The annual flux of tropospheric water into the stratosphere is set to 788 Mt (Yang and Tung, 1996). In the stratosphere further 63.9 Mt H₂O (and 0.31 Mt H₂) is net produced due to the oxidation of CH₄. The calculated annual CH₄ destruction rate is 30 Mt yr⁻¹. This value is slightly lower than the (40 ± 10) Mt yr⁻¹ often reported (Crutzen, 1995; Lelieveld et al., 1998), but agrees with Gettelmann et al. (1998) and exceeds earlier values given by Crutzen (1991) and Khalil et al. (1993). The calculated ratios between H₂O

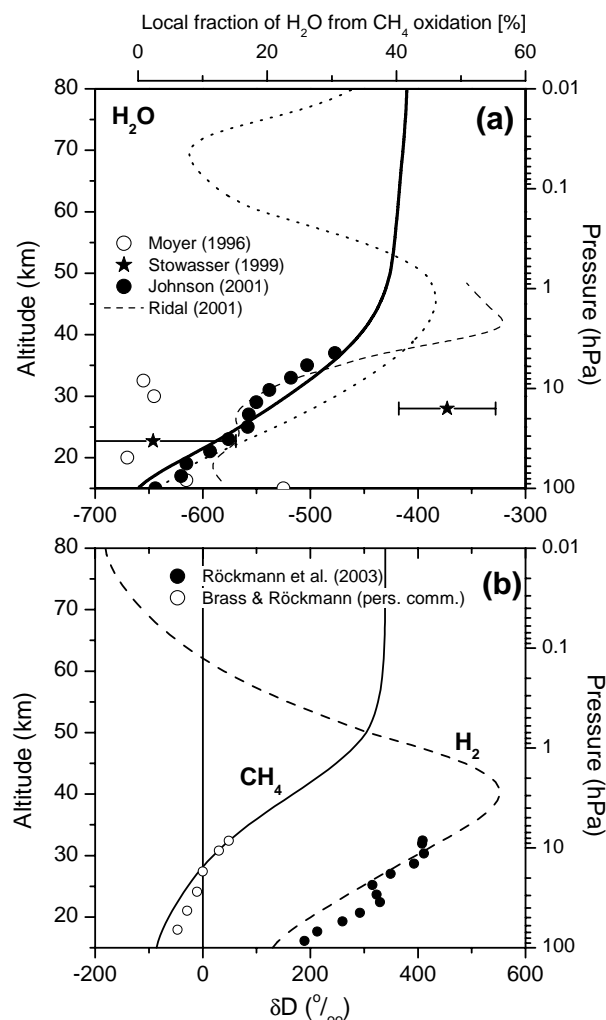


Fig. 3. Calculated vertical profile of δD in H₂O (graph a, thick line), and CH₄ and H₂ (graph b) compared to measurements. **(a)** Dotted line: δD of freshly produced H₂O. Open circles: ATMOS FTIR data of near-global latitudinal coverage (Moyer et al., 1996). Full circles: Smithsonian Astrophysical Observatory's far-infrared data by Johnson et al. (2001a). Stars: Balloon-borne MIPAS data inside the Arctic vortex at 68°N (Stowasser et al., 1999). Dashed line: 1-D model result by Ridal et al. (2001). Upper x-axis indicates the approximate fraction of H₂O from the CH₄ oxidation inferred from the $\delta D(H_2O)$ value (explanation, see Sect. 6.3). **(b)** Full and open circles: Laboratory mass-spectrometer data of in-situ samples.

and H₂ production and CH₄ loss for the entire middle atmosphere are:

$$\frac{P(H_2O)}{L(CH_4)} = 1.90 \quad \text{and} \quad \frac{P(H_2)}{L(CH_4)} = 0.10 \quad (5)$$

Using a coupled chemistry/dynamical model (LeTexier et al., 1988) derived $P(H_2O)/L(CH_4)=1.6$ which is in agreement with satellite observations by Hanson and Robinson (1989). More recent in situ measurements indicated higher values of 1.94 ± 0.27 (Dessler et al., 1994), 1.82 ± 0.21 (Engel et al.,

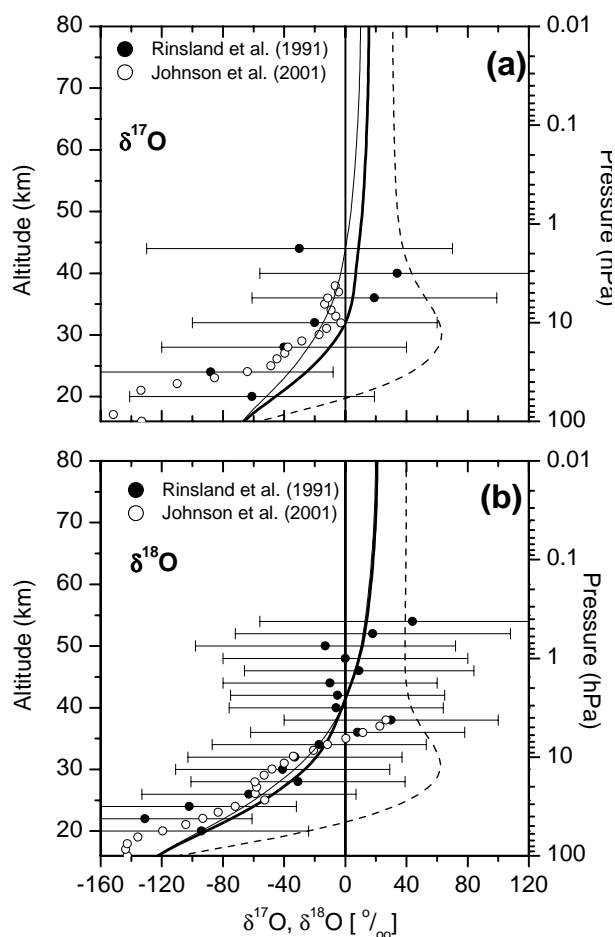


Fig. 4. Calculated vertical profiles of $\delta^{17}\text{O}(\text{H}_2\text{O})$ (graph a) and $\delta^{18}\text{O}(\text{H}_2\text{O})$ (graph b) compared to ATMOS Spacelab 3 infrared solar spectra near 30°N (Rinsland et al., 1991) and FTIR balloon-borne data at 33° and 68°N (Johnson et al., 2001). Thick straight lines: base run. Dashed lines: Oxygen exchange reaction (R38) ($\text{NOQ} + \text{H}_2\text{O} \rightleftharpoons \text{NO}_2 + \text{H}_2\text{Q}$) is considered at its estimated upper limit. Thin straight lines: Oxygen exchange reactions (R39) ($\text{QH} + \text{O}_2 \rightleftharpoons \text{OH} + \text{OQ}$) and (R40) ($\text{HOQ} + \text{O}_2 \rightleftharpoons \text{HO}_2 + \text{OQ}$) are considered at their estimated upper limits.

1996), 1.973 ± 0.003 (Hurst et al., 1999), and 1.975 ± 0.030 (Zöger et al., 1999), which are in reasonable agreement with our model results.

Interestingly, although each CH_4 molecule finally results in the formation of almost two H_2O molecules (Eq. 5), most hydrogen atoms in CH_4 make the detour via other gases to H_2O , as demonstrated in Fig. 6. Only $\sim 15\%$ of all H_2O molecules are formed directly from one of the four H atoms of CH_4 or intermediate products in the CH_4 destruction chain (such as formaldehyde, CH_2O), i.e., are produced via reactions:

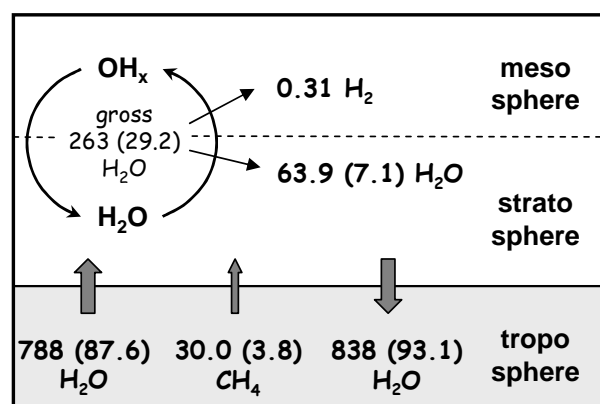


Fig. 5. Middle atmospheric budget of H_2O . Numbers are mass fluxes in Mt yr^{-1} . Numbers in parenthesis are fluxes of H_2 in Mt yr^{-1} . The H_2O flux into the stratosphere is adopted from Yang and Tung (1996), other numbers are model results.

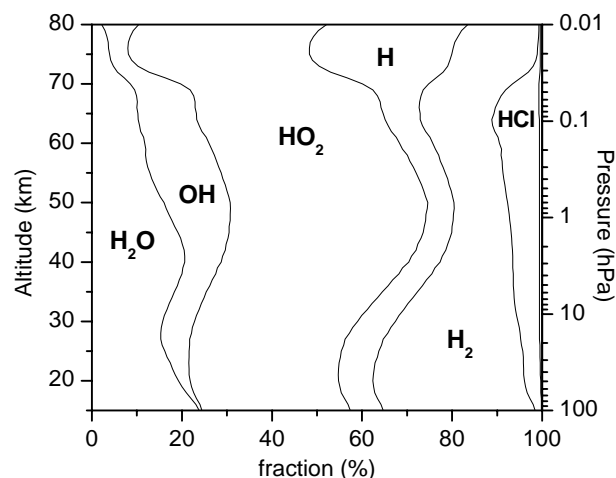


Fig. 6. Calculated percentage fraction of hydrogen atoms that are transferred during the initial oxidation reaction of CH_4 either to H_2O , OH , HO_2 , H , H_2 , or HCl .

The other $\sim 85\%$ of the H atoms in CH_4 are incorporated first in OH , HO_2 , H_2 , H , or HCl , before ending up in H_2O . This detour the H atoms take from CH_4 to H_2O certainly affects not only the isotope composition of the final product H_2O , but also that of the intermediate species (OH , HO_2 , HCO , H_2 , H , HCl etc.).

Figure 7 presents the vertical profile of H_2O production $P(\text{H}_2\text{O})$ and loss $L(\text{H}_2\text{O})$. Both $P(\text{H}_2\text{O})$ (dominated by the reaction $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ – Kaye, 1990) and $L(\text{H}_2\text{O})$ (more than 99% of which are due to the reaction of $\text{H}_2\text{O} + \text{O}(^1\text{D}) \rightarrow 2\text{OH}$) peak at $\sim 38\text{ km}$ altitude. The net rate, $P(\text{H}_2\text{O}) - L(\text{H}_2\text{O})$, amounts to $\sim 27\%$ of $P(\text{H}_2\text{O})$ only. It shows a wide maximum centred at $35\text{--}40\text{ km}$, that is $\sim 5\text{ km}$ above the maximum of the CH_4 loss rate (for better comparison $2 \times L(\text{CH}_4)$ is shown, dotted line). This again emphasises that during the oxidation of CH_4 most H atoms are first

incorporated in intermediate species (where the longer lived ones H₂, HCl, and HNO₃ experience spatial redistribution) before ending up in H₂O, and that a considerable turnover of H₂O molecules occurs in the middle atmosphere which significantly exceeds the net production of H₂O.

6.2 The chemical lifetimes of H₂O, $\delta D(H_2O)$, $\delta^{17}O(H_2O)$, and $\delta^{18}O(H_2O)$

Division of the local H₂O concentration by the local H₂O loss rate $L(H_2O)$ yields the chemical lifetime of H₂O, $\tau(H_2O)$, at a certain altitude (Fig. 7b). As the same reactions control the loss of HDO molecules, the chemical lifetime of HDO, $\tau(HDO)$, is identical with $\tau(H_2O)$. In the entire middle atmosphere $\tau(H_2O)$ or $\tau(HDO)$, respectively, (like $\tau(CH_4)$) exceeds the vertical transport time scale H^2/K_z (H being the local scale height and K_z the vertical eddy diffusion coefficient). That is, neither H₂O nor HDO is in photochemical equilibrium in the middle atmosphere. Only between 35 and 50 km altitude, the transport time scale almost compares with the photochemical lifetime of H₂O (and HDO), in agreement with (LeTexier et al., 1988). Below 35 km, $\tau(H_2O)$ and $\tau(HDO)$ exceeds ~ 5 years.

Consider moreover, that the influence of in-situ H₂O production due to CH₄ oxidation on $\delta D(H_2O)$ is small below ~ 30 km, too. This can be seen in Fig. 7a, when the net H₂O production (black line) displayed in molecules $cm^{-3} s^{-1}$ is divided by the pressure, which gives the H₂O production in ppmv s^{-1} . This number peaks at 45 km and is small below ~ 30 km.

The latter conclusion and the long chemical lifetime implies that below 30–35 km the H₂O mixing ratio as well as its δD value is largely dominated by transport, i.e. by vertical transport for the present 1-D model. Thus, between the tropopause and 30–35 km the H₂O mixing ratio and its δD value is determined by (vertical) mixing of two reservoirs, the one at the tropopause which is controlled by (physical) fractionation processes in the troposphere, and the second above 30–35 km which is determined by the dominant H₂O loss reaction (R30).

For the oxygen isotopologues $\delta^{17}O(H_2O)$ and $\delta^{18}O(H_2O)$, additional oxygen exchange of H₂O with other gases (Reactions R34 and R38) causes somewhat shorter lifetimes of the $\delta^{17}O$ and $\delta^{18}O$ signature of the stratospheric water vapour. Moreover, the vital recycling of water (via HO_x species) only weakly affects the $\delta D(H_2O)$ value, because H₂O is the major hydrogen reservoir in the mesosphere. This is not the case for $\delta^{17}O(H_2O)$ and $\delta^{18}O(H_2O)$, where the many intermediate species involved in the H₂O recycling process exchange oxygen atoms with the other major oxygen “reservoirs” O₂ and O₃.

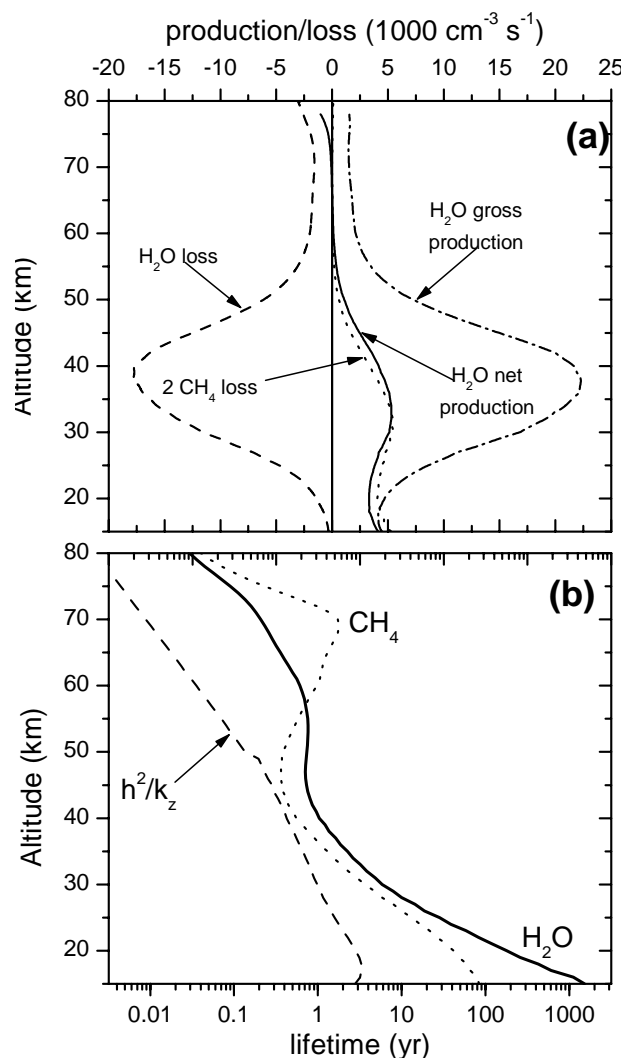


Fig. 7. (a) calculated vertical profiles of H₂O production and loss rates in the middle atmosphere. For comparison, the double CH₄ loss rate is shown (as almost two H₂O molecules are net produced for each oxidised CH₄ molecule, see Eq. 5). (b) comparison of the photochemical lifetime of H₂O and CH₄ with the transport time scale (h^2/k_z , with h : atmospheric scale height and k_z : vertical eddy diffusion coefficient).

6.3 $\delta D(H_2O)$ as tracer for CH₄ oxidation

Tropospheric H₂O is imported into the stratosphere with $\delta D(H_2O) \approx -660\text{‰}$ (Moyer et al., 1996; Johnson et al., 2001; Kuang et al., 2003; McCarthy et al., 2004). Tropospheric CH₄ carries much higher δD values of roughly -86‰ (Quay et al., 1999) into the stratosphere. The vertically increasing contribution of H₂O produced by the oxidation of CH₄ is described by the upper x-axis of Fig. 3. It shows the local fraction of H₂O from CH₄ oxidation \mathcal{F} , that is the ratio between the difference of the local $\delta D(H_2O)$ value to the tropopause value (-660‰) and the difference of the $\delta D(H_2O)$ from the

CH₄ oxidation (set to −86‰) and the δD(H₂O) tropopause value, i.e.,

$$\mathcal{F} = \frac{\delta D(\text{H}_2\text{O}) - (-660\text{‰})}{-86\text{‰} - (-660\text{‰})} \quad (6)$$

Figure 3 indicates that ~40% of the water vapour present above 40 km originate from the oxidation of CH₄. For simplicity, we have set δD(CH₄) constant, although in reality it varies with altitude (Fig. 3b). The influence of this simplification is surprisingly weak. This has two reasons. First, the contributions of the three main CH₄ loss reactions (R1–R3) are comparable throughout the middle and upper stratosphere (where the major CH₄ loss occurs). Second, due to the long chemical lifetime of H₂O (and HDO), spatial redistribution smears out the anyway weak vertically changing δD(H₂O) source signature.

Unfortunately, this fact also documents that the δD(H₂O) value does not constitute a sensitive measure for quantifying the partitioning of the different CH₄ loss reaction chains, contrary to its initial assumption.

Another surprising feature is that both, the δD value of the source molecule CH₄ and the one of the end product H₂O increase with altitude (Fig. 3), although mass conservation for δD at a first glance suggests the opposite behaviour. In all methane oxidation reactions the most abundant CH₄ reacts faster than the isotopically substituted CH₃D (Sect. 3). Hence, the remaining CH₄ is continuously enriched in D/H with altitude. The D/H ratio of the freshly formed H₂O is certainly much lower (dotted line) but is still higher than the D/H ratio of the H₂O lofted from below. Thus, both the δD value of CH₄ and of freshly produced H₂O increases with altitude. Note that for an isotope mass balance the δ values must be multiplied with the concentrations. Here, the concentration of the “D-richer” source CH₄ decreases and the concentration of the D-depleted product H₂O increases. Thus, mass balance is achieved although both δ values increase.

6.4 δ¹⁷O(H₂O) and δ¹⁸O(H₂O) as tracer for transport and chemistry

As outlined in Sect. 3, the oxygen isotope signature of middle atmospheric water vapour is determined by the partitioning of four oxygen isotope sources: (1) mass-dependently fractionated (MDF) H₂O imported from the troposphere, (2) mass-independently fractionated (MIF) H₂O formed as a final product of the oxidation of CH₄, (3) MIF carrying H₂O from the recycling of H₂O via the HO_x family and (4) oxygen atom exchange between H₂O and other gases.

The δ¹⁷O and δ¹⁸O values of source (1), i.e. of H₂O imported from the troposphere, are about −67‰ and −128‰, respectively (see Sect. 4.6). The δO values of water produced by the isotope sources (2) to (4) are controlled by the respective educt molecules and the kinetic isotope fractionation factor KIE of the relevant reaction. As outlined by Kaye (1990) and confirmed by our calculations, more than 99% of

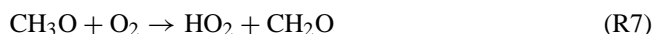
all H₂O molecules generated in the middle atmosphere are due to hydrogen abstraction reactions by OH. Thus, the isotope sources (2) and (3) will show the O isotope signature of OH at the respective altitude. H₂O itself undergoes oxygen isotope exchange (i.e. isotope source 4) with OH (R34) and NO₂ (R41, Table 5). Reaction (R34) is too slow to significantly affect the isotope composition of H₂O. The rate constant of Reaction (R38) was not quantified yet; its potentially considerable impact is addressed in Sect. 6.5.

In conclusion, the modification of the oxygen isotope composition of middle atmospheric H₂O is controlled by the oxygen isotope composition of OH. For this reason, the oxygen isotope signature of the different OH sources is studied next. Reaction chains where OH is converted into HO₂ and back into OH without breaking the initial OH bond constitute a zero cycle with respect to the oxygen isotopic composition. Thus, only reactions forming new OH bonds need to be considered.

6.4.1 The formation of new OH bonds

The influence of the most important reactions forming new OH bonds are displayed in Fig. 8a. Four classes of reactions, distinguished by the O isotope signal transferred, form new OH_x bonds:

(i) HO_x that receives the oxygen isotope signature from molecular oxygen via



Reactions (R7) and (R12) are part of the CH₄ oxidation chain and only play a role below 40 km. Reaction (R13) clearly dominates the formation of new OH bonds in the mesosphere. In addition, oxygen isotope exchange between HO_x and O₂ may occur (Reactions R39 and R40) the influence of which are discussed in Sect. 6.5.

(ii) HO_x that receives the oxygen isotope signature from MIF carrying ozone via



which is important above 40 km only. Although O₃ also influences the isotope composition of HO₂ via OH+O₃→HO₂+O₂, new OH bonds are not formed. The reason is that the oxygen atom that OH receives from O₃ is lost again, simply because HO₂ is an asymmetric molecule (H–O–O).

(iii) HO_x that receives the oxygen signature from MIF carrying O(¹D) and, in the case of Reaction (R30), from H₂O:

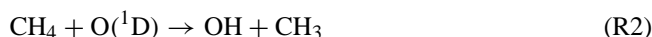


Table 6. Percentage origin of oxygen isotopes of freshly produced H₂O averaged over stratosphere and mesosphere.

Oxygen Isotope Source		base run		considering R39–R41		considering R38	
Species	isotope signature	stratosph.	mesosph.	stratosph.	mesosph.	stratosph.	mesosph.
O ₂	MDF ^a	79.5	74.6	98.1	77.5	70.0	74.6
O ₃	MIF ^b	16.5	25.3	1.5	22.4	26.6	25.3
O(¹ D)	MIF ^b	2.1	0.0	0.2	0.0	1.8	0.0
others		1.9	0.1	0.2	0.1	1.6	0.1

^a MDF = mass-dependently fractionated^b MIF = mass-independently fractionated

while the most important of them, Reaction (R30), plays only a modest role between 30 and 45 km.

(iv) HO_x that receives the oxygen isotope signature from NO_x:



while the oxygen isotope composition of NO_x is controlled by reactions with the O₂ and O₃ reservoirs (Sect. 4.4).

6.4.2 The origin of oxygen atoms incorporated in H₂O

On the basis of Sect. 6.4.1, the influence of each oxygen source (O₂, O₃, O(¹D), and NO_x) for the oxygen isotope composition of freshly produced H₂O is assessed. As demonstrated in Fig. 8 and listed in Table 6, molecular oxygen clearly dominates as source of oxygen atoms transferred to water vapour in the entire middle atmosphere. In the model base run (R38 to R41 are omitted), of all oxygen isotopes incorporated in H₂O in stratosphere and mesosphere, respectively, ~78% and ~70% stem from O₂, ~17% and ~30% from O₃, ~2% and ~0% from O(¹D), and ~2% and ~0% from other gases such as HNO₃ or H₂O itself (Fig. 8). Another interesting feature is that in the stratosphere ~50% of the overall oxygen isotope transfer to H₂O proceeds in two steps, that is from O₂ and O₃ to NO_x and then from NO_x via HO_x to H₂O.

This oxygen isotope source partitioning (Fig. 8, Table 6) is reflected in the strongly structured vertical profiles of δ¹⁷O(H₂O) and δ¹⁸O(H₂O) of freshly produced H₂O (Fig. 9). Two maxima occur, both due to oxygen atom transfer from O₃ to H₂O. In the stratosphere, it is the oxygen transfer chain O₃ $\xrightarrow{\text{O}}$ NO_x $\xrightarrow{\text{O}}$ HO_x $\xrightarrow{\text{O}}$ H₂O. In the mesosphere with the high concentrations of atomic hydrogen, it is caused by H+O₃→OH+O₂ (Reaction R14) and subsequent O transfer from OH to H₂O.

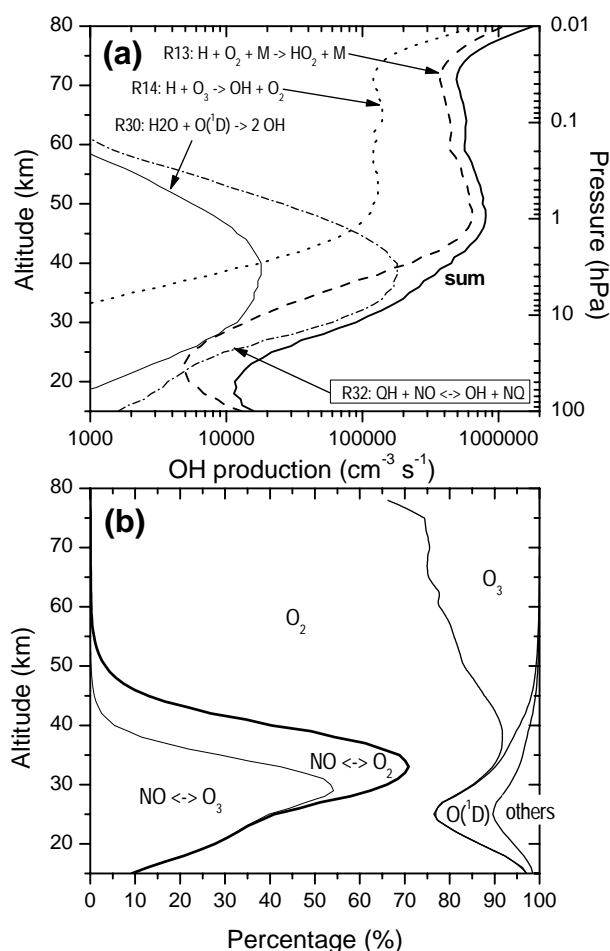


Fig. 8. (a) Four most important reactions that lead to the formation of new OH bonds. (b) Percentage fraction of oxygen atoms originating from the “reservoirs” O₂, O₃, and O(¹D) in freshly produced H₂O. Thick straight lines separate the three different reservoirs. In the stratosphere, considerable oxygen transfer from O₂ and O₃ to H₂O occurs via the NO_x family (grey areas).

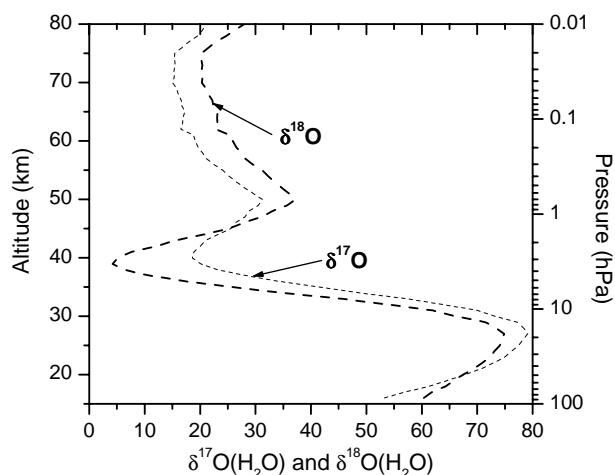


Fig. 9. Vertical profiles of $\delta^{17}\text{O}(\text{H}_2\text{O})$ and $\delta^{18}\text{O}(\text{H}_2\text{O})$ of freshly produced H₂O.

6.4.3 $\Delta^{17}\text{O}(\text{H}_2\text{O})$ as a tracer of MIF transfer from O₃ to H₂O

The last Sect. 6.4.2 revealed that the pathway of MIF from O₃ to H₂O is different compared to the one from O₃ to CO₂. CO₂ is assumed to receive the MIF signal exclusively from O(¹D) (produced by the photolysis of O₃) via the short-lived intermediate CO₃′ (Yung et al., 1991, 1997; Barth and Zahn, 1997). In the case of H₂O, O(¹D) is only weakly involved in the oxygen isotope transfer (Table 6). In the stratosphere water vapour receives only ~15% of its MIF signal from O(¹D). In the mesosphere O(¹D) does not play any role at all.

As indicated in Fig. 8, in the stratosphere MIF transfer from O₃ to H₂O basically proceeds in three steps, first MIF transfer from O₃ to NO_x species (via reaction NO-1: NO+O₃→NO₂+O₂, Sect. 4.5), then from NO_x to OH_x and finally transfer to H₂O due to H-abstraction by OH. This quite efficient oxygen transfer chain leads to peaking $\Delta^{17}\text{O}(\text{H}_2\text{O})$ values of ~10‰ around ~32 km altitude (Fig. 10). In the mesosphere, NO_x species are not involved. There, the entire MIF transfer from O₃ to HO_x (and from there to H₂O) proceeds via Reaction (R14): H+O₃→OH+O₂.

6.5 Sensitivity study: Influence of additional oxygen isotope exchange reactions

The results discussed so far constitutes the “base run” in which the already quantified (oxygen) isotope exchange reactions (R32) to (R37) (Table 5) were considered. The last Sect. 6.4 actually revealed the importance of the oxygen isotope exchange reaction (R32) (see Fig. 8) for the oxygen isotope composition of OH and thus freshly produced H₂O.

If the three further, still unquantified exchange reactions with the O₂ reservoir (R39) to (R41) are considered at their estimated upper limit (Table 5), $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ of water

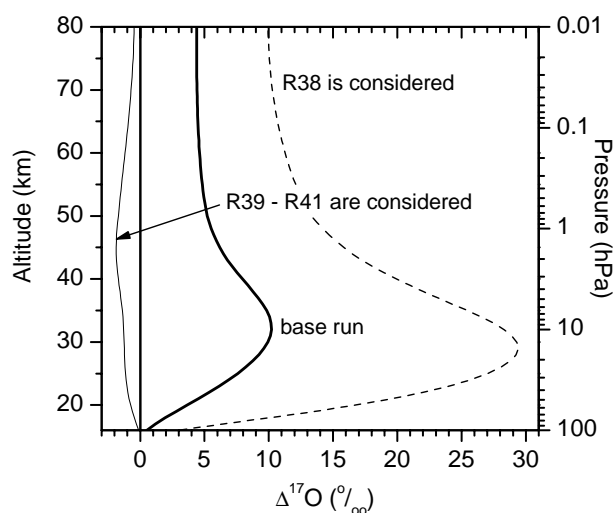


Fig. 10. Calculated vertical profile of $\Delta^{17}\text{O}(\text{H}_2\text{O})$. Thick straight line: base run. Dashed line: Oxygen exchange reaction (R38) ($\text{NO} + \text{H}_2\text{O} \rightleftharpoons \text{NO}_2 + \text{H}_2\text{O}$) is considered at its estimated upper limit. Thin straight line: Oxygen exchange reactions (R39) ($\text{QH} + \text{O}_2 \rightleftharpoons \text{OH} + \text{OQ}$) and (R40) ($\text{HOQ} + \text{O}_2 \rightleftharpoons \text{HO}_2 + \text{OQ}$) are considered at their estimated upper limits.

vapour (and OH) are slightly lower (thin lines in Fig. 4), but the MIF signal is completely washed out (Fig. 10).

On the contrary, if the isotope exchange reaction (R38) ($\text{NO} + \text{H}_2\text{O} \rightleftharpoons \text{NO}_2 + \text{H}_2\text{O}$) is considered at the rate measured forty years ago by Jaffe and Klein (1966), the enrichment in $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ (Fig. 4) as well as the MIF signal (Fig. 10) strongly increases in the stratosphere and reaches values of $\Delta^{17}\text{O}(\text{H}_2\text{O}) \approx 30\text{‰}$ at ~29 km altitude.

This strong sensitivity to isotope exchange reactions documents the urgent need for better quantified rate constants of the relevant reactions.

7 Conclusions

Application of a simple 1-D isotope chemistry box model demonstrates that a significant number of chemical reactions with diverse gases cause considerable fractionation of all three stable isotope ratios D/H, $^{17}\text{O}/^{16}\text{O}$, and $^{18}\text{O}/^{16}\text{O}$ in middle atmospheric water vapour relative to values at the tropopause. This makes a description much more complicated compared to other trace gases such as CO₂, CH₄, and N₂O.

$\delta\text{D}(\text{H}_2\text{O})$ was modelled to increase from −660‰ at the tropopause to −410‰ above 40 km, which is in excellent agreement with the observations. This increase by ~250‰ corresponds to a fraction of ~40% of H₂O produced as end product of the oxidation of CH₄. Although the D fractionation factors of the individual CH₄ oxidation reactions with OH, O(¹D), and Cl differ strongly, the $\delta\text{D}(\text{H}_2\text{O})$ value turned out to be no sensitive tracer to distinguish between

the different CH₄ oxidation chains. This has two reasons. First, the major CH₄ loss occurs in the middle and upper stratosphere where the reactions with O(¹D) which comes along with weak isotope fractionation dominates. Second, the chemical lifetime of H₂O is long in the middle atmosphere. This allows for significant redistribution and thus weakening of spatial gradients of δD(H₂O).

The results for the oxygen isotope ratios ¹⁷O/¹⁶O, and ¹⁸O/¹⁶O are less robust, because of the many reactions involved in the oxygen isotope transfer from the reservoirs to H₂O and the many badly or not quantified isotope fractionation factors and oxygen isotope exchange reactions. In the base run, where the Reactions (R38), (R39) and (R40) are not considered, δ¹⁷O(H₂O) and δ¹⁸O(H₂O) are calculated to increase relative to the tropopause by up to ~85‰ and ~145‰, respectively, which is also in agreement with the observations. Fractionation of the oxygen isotope ratios in H₂O was demonstrated to be determined almost exclusively by the isotope signature of OH. The oxygen isotopic composition of OH, in turn, is mainly controlled by the one of O₂ that is mass-dependently fractionated (MDF). In the stratosphere and mesosphere, respectively, ~78 and ~70% of all oxygen atoms transferred to H₂O stem from O₂, while ~17 and ~30% originate from O₃ that is mass-independently fractionated (MIF). As a result, the calculated MIF signal of H₂O is only modest and reaches values of Δ¹⁷O(H₂O)=10‰ at 30–35 km altitude.

However, if beyond the base run, further badly quantified oxygen isotope exchange reactions with O₂ (R39 and R40) are considered at their estimated upper limit, the MIF signature completely vanishes in middle atmospheric H₂O. In contrast, if the isotope exchange reaction of H₂O with NO₂ (Reaction R38) is considered, the MIF signal reaches high values of Δ¹⁷O(H₂O)=30‰ around 29 km. Indeed and in any case, the transfer of the MIF signature in O₃ to OH and H₂O proceeds primarily via NO_x species in the stratosphere and directly via the reaction of H+O₃→OH+O₂ in the mesosphere. That is, the MIF transfer from O₃ to H₂O is quite different from the one from O₃ to CO₂ where it proceeds via O(¹D) and the intermediate complex CO₃^{*}.

The largest unknowns in our calculations are the unquantified reaction rates of a few oxygen isotope exchange reactions, in particular of OH_x and NO_x with O₂, and the many unquantified isotope fractionation factors of the reactions involved in the isotope transfer to H₂O. In this respect, the most urgent need in this research field is the development of more precise techniques to measure the isotope composition of water vapour both in the laboratory and atmosphere.

Finally, the calculated MIF signal transferred to HO_x and thus to H₂O is only half as large as the one determined by Lyons (2001). This discrepancy arises from the different Δ¹⁷O signatures assumed for the asymmetric O₃ molecule and O(¹D). Lyons (2001) used (i) the branching ratios of 0.43 and 0.57 for δ¹⁸O in the reaction of O+QO→OQO and QOO as measured by Janssen

et al. (1999) for δ¹⁷O, too, and (ii) the isotope fractionation factors for this reaction measured by Mauersberger et al. (1999). This assumption led to Δ¹⁷O values of asymmetric O₃ of Δ¹⁷O(QOO)=~85‰, and together with the mean Δ¹⁷O values of O₃ of Δ¹⁷O(O₃)=~38‰, to Δ¹⁷O values of symmetric O₃ of Δ¹⁷O(OQO)=-50‰ only (because Δ¹⁷O(O₃)=2/3 Δ¹⁷O(QOO)+1/3 Δ¹⁷O(OQO)). Such a strong difference in Δ¹⁷O between asymmetric and symmetric ozone is unlikely (C. Janssen, personal communication). In contrast, we assumed identical ratios of the enrichments of δ¹⁷O and δ¹⁸O in QOO and OQO. That is, in the stratosphere we apply mean Δ¹⁷O values of 34‰ for O₃, which is in agreement with Lyons (2001), but Δ¹⁷O values of 39‰ for QOO and 25‰ for OQO.

Acknowledgements. We thank U. Platt for his scientific assistance during the early preparation phase.

Edited by: U. Pöschl

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